

**S1 Table. MALDI-TOF MS and HPLC analysis of substrates 1–27.** MALDI-TOF mass spectra were performed using a Bruker UltraflexExtreme MALDI TOF/TOF instrument and analysed with the Bruker Daltonics flexAnalysis software. For peptide/peptoid analysis, sinapic acid was used as a matrix and positive ion mass spectra were recorded. HPLC analyses were performed on an Agilent 1100 analytical system equipped a Supelco Discovery<sup>®</sup> C18 column (5  $\mu$ m, 5 cm) coupled to a Polymer laboratories 100 ES evaporative light scattering detector (ELSD). Eluting from 5% A (H<sub>2</sub>O + 0.1% formic acid) to 95% (MeOH + 0.1% formic acid) over 8 min, followed by isocratic 95% B for 1 min, at a flow rate of 1 mL/min. Semipreparative HPLC purifications were performed on an Eclipse XDB-C18 column (9.4 x 250 mm, 5  $\mu$ m), at a flow rate of 2 mL/min, with detection/collection at 254 nm. The following gradient was used: 5 to 50 % A over 6 min, 50 to 100% B for 30 min.

	Sequence	MW [calc.]	MALDI-TOF	HPLC purity (%)
1	DEVD	(M+H) <sup>+</sup> 2845.8	2845.1	100
2	DEVD	(M+H) <sup>+</sup> 2837.7	2837.1	92
3	DEVD	(M+H) <sup>+</sup> 2883.7	2883.9	75
4	DPVD	(M+H) <sup>+</sup> 2813.8	2813.3	93
5	DGVD	(M+H) <sup>+</sup> 2774.6	2774.2	97
6	DAVD	(M+H) <sup>+</sup> 2788.6	2788.3	99
7	DLVD	(M+H) <sup>+</sup> 2829.8	2829.4	96
8	DNVD	(M+H) <sup>+</sup> 2829.8	2829.4	98
9	DVVD	(M+H) <sup>+</sup> 2816.6	2816.3	99
10	DGPD	(M+TFA-H) <sup>+</sup> 2881.7	2881.6	93
11	DAPD	(M+TFA-H) <sup>+</sup> 2895.7	2895.5	95
12	DLPD	(M+TFA-H) <sup>+</sup> 2937.8	2934.3	90
13	DNPD	(M+TFA-H) <sup>+</sup> 2938.7	2937.4	94
14	DVPD	(M+TFA-H) <sup>+</sup> 2923.7	2923.0	100
15	dgvd	(M+Na+K) <sup>+</sup> 2832.7	2832.4	100
16	davd	(M+Na+K) <sup>+</sup> 2847.7	2847.5	100
17	dlvd	(M+Na+K) <sup>+</sup> 2889.7	2889.3	100
18	dnvd	(M+Na+K) <sup>+</sup> 2890.7	2890.3	100
19	dvvd	(M+Na+K) <sup>+</sup> 2875.7	2875.4	100
20	dgpd	(M+Na+K) <sup>+</sup> 2831.7	2831.4	100
21	dapd	(M+Na+K) <sup>+</sup> 2845.7	2845.5	100
22	dlpd	(M+Na+K) <sup>+</sup> 2887.7	2887.4	100
23	dnpd	(M+Na+K) <sup>+</sup> 2888.7	2888.3	100
24	dvpd	(M+Na+K) <sup>+</sup> 2873.7	2873.4	100
25	DLPD-Ahx-k	(M + H) <sup>+</sup> 2827.7	2827.5	100
26	DLPD-Ahx-K(Me)	(M + 2Na - H) <sup>+</sup> 2883.6	2883.9	100
27	DLPD-K-Ahx	(M + H) <sup>+</sup> 2827.7	2827.7	100